Structure-Function Relationships Affecting the Insecticidal and Miticidal Activity of Sugar Esters

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ABSTRACT Synthetic sugar esters are a relatively new class of insecticidal compounds that are produced by reacting sugars with fatty acids. The objective of this research was to determine how systematic alterations in sugar or fatty acid components of sugar ester compounds influenced their insecticidal properties. Sucrose octanoate, sorbitol octanoate, sorbitol decanoate, sorbitol caproate, xylitol octanoate, xylitol decanoate and xylitol dodecanoate were synthesized and evaluated against a range of arthropod pests. Dosage-mortality studies were conducted on pear psylla (*Cacopsylla pyricola* Foerster) on pear, tobacco aphid (*Myzus nicotianae*) Blackman and tobacco hornworm (*Manduca sexta* [Johannson]) on tobacco, and twospotted spider mite (*Tetranychus urticae* Koch) on apple in laboratory bioassays. These sugar esters were compared with insecticidal soap (M-Pede, Dow AgroSciences L.L.C., San Diego, CA), to determine how toxicologically similar these materials were against the arthropod pests. Substitutions in either the sugar or fatty acid component led to significant changes in the physical properties and insecticidal activity of these compounds. The sugar esters varied in their solubility in water and in emulsion stability, yet, droplet spread upon pear leaves occurred at low concentrations of 80–160 ppm and was strongly correlated with psylla mortalities ($R^2 = 0.73$). Sequentially altering the sugar or fatty acid components from lower to higher numbers of carbon chains, or whether the sugar was a monosaccharide or disaccharide did not follow a predictable relationship to insecticidal activity. Intuitively, changing the hydrophile from sorbitol (C_6) to xylitol (C_5) would require a decrease in lipophile chain length to maintain hydrophilic-lipophilic balance (HLB) relationships, yet an increase in lipophile chain length was unexpectedly needed for increasing insecticidal activity. Thus, the HLB of these materials did not correlate with pear psylla mortalities. Initial insect bioassays and dosage-mortality data found significant differences among sugar ester compounds' toxicity to the range of arthropod species. Sucrose octanoate high in monoester content had the highest activity against the range of arthropod pests at low concentrations of 1200–2400 ppm. No single chemical structure for the xylitol or sorbitol esters were optimally effective against the range of arthropods we tested and sorbitol octanoate and xylitol decanoate had the highest insecticidal activity of this group. All of the sugar ester materials produced high *T. urticae* mortalities on apple at very low concentrations of 400 ppm. Overall, most of the sugar esters that were examined had superior insecticidal activity compared with insecticidal soap. Sugar ester chemistry offers a unique opportunity to design an insecticide or miticide specific to certain arthropod pests which would be valuable in crop integrated pest management (IPM) programs. Sucrose esters are currently used as additives in the food industry which makes them especially attractive as safe and effective insecticides.

KEY WORDS biopesticide, biorational insecticide, polyol esters, surfactant, acyl sugar, sucrose octanoate

SUGAR ESTERS, ALSO KNOWN as acyl sugars or polyol esters, are a class of compounds produced by reacting sugars, including reduced sugars, with aliphatic or aromatic acids. Sucrose esters occur naturally in plants and are being commercially synthesized for use in the food industry (Chortyk et al. 1996). The glandular trichomes of wild tobacco, *Nicotiana gossei* Domin, have been known to possess insecticidal materials for some time (Thurston and Webster 1962). Yet, it was not until the early 1990s that sucrose esters were determined to be the primary insecticidal compounds within these glandular trichomes (Buta et al. 1993, Pittarelli et al. 1993). Synthetic sucrose esters that are similar in structure to those that naturally occur in *N. gossei* have comparable insecticidal activity (Chortyk et al. 1996). Both natural and synthetic sucrose esters have been shown to have contact toxicity with very

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rapid knock-down ability to soft-bodied arthropods including mites, aphids, whitefly and psyllids (Neal et al. 1994, Puterka and Severson 1995, Liu et al. 1996). Feeding and ovipositional deterrence to mites (Neal et al. 1994) and whiteflies (Liu and Stansly 1995) have also been demonstrated with sucrose esters.

There are eight free hydroxyl groups on a sucrose molecule that can be esterified during sucrose ester synthesis. Differing methods of synthesis can influence whether the resulting sucrose ester product is comprised primarily of mono-acyl sucrose (Farone et al. 2002) or a mixture of di- and tri-acyl sucroses (Chortyk et al. 1996). Previous research has established that di-acyl sucrose esters have the greatest insecticidal activity while mono- or tri-acyl sucrose esters had little activity (Chortyk et al. 1996). Furthermore, these researchers found that the sugar esters containing $C_{9,}$ C_{10}, and C_{12} fatty acids produced low aphid mortalities compared with those containing C_7 and C_8 fatty acids. Yet, field evaluations found no differences in whitefly control when comparing sucrose esters comprised of 7, 8, 9, or 10 chain fatty acids (Liu et al.1996).

Further research is needed for a better understanding of the structure-function relationships that influence the insecticidal activity of sugar esters. Our study examines how varying the sugar and fatty acid components of sugar esters influences their insecticidal activity against a range of insect species. The performance of these compounds were compared with a common insecticidal soap,

M-Pede (Dow AgroSciences, L.L.C., Indianapolis, IN), to determine how toxicologically similar these materials were to arthropod pests.

Materials and Methods

Physical Properties of Sugar Esters. The sugar ester compounds, henceforth called sugar esters, that we examined were sucrose octanoate, sorbitol octanoate, sorbitol caproate, sorbitol decanoate, xylitol octanoate, xylitol dodecanoate, and xylitol decanoate. These compounds were produced by Applied Power Concepts, Inc., Anaheim, CA, that used the manufacturing processes described by Farone et al. (2002) to synthesize the xylitol and sorbitol esters or by Farone and Serfass (1998) to produce sucrose octanoate high in monoester content (>60%). The purity of these compounds ranged from 88 to 94% active ingredient (AI) with the inert ingredients being unreacted sugar. The insecticidal soap, M-Pede, was commercially available and contained 49% (AI) potassium salts of fatty acids. Stock solutions of all the experimental materials were prepared at 40% (AI) (vol:vol) before the series of dilutions were made. The sugar ester compounds were selected to provide the sugar-fatty acid combinations that enabled comparisons to be made between sugar esters containing reduced sugars of different molecule size (xylitol = C_5, sorbitol = C_6) and disaccharide sugars (sucrose = C_{12}), and between sugar esters containing C_6 (caproate), C_8 (octanoate), C_{10} (decanoate) and C_{12} (dodecanoate) fatty acids.

The physical properties assessed for each sugar ester were color, physical state of the technical material (80–94% [AI]), solubility in water, stability of a 2,400 ppm (AI) sugar ester solution in water, and sugar ester concentration at which droplets spread freely on pear leaves at a temperature of 25 ± 2°C. Sugar ester solubility in water was determined by adding 0.6 g of sugar ester material (40% [AI]) in 100 ml of water (25°C) to make a 2,400-ppm solution and classifying each material by the ease of making an emulsion. The classifications were: excellent = readily mixed with water and hand shaking 30 s made a uniform emulsion; good = mixed with difficulty and vigorous hand shaking for 1 min produced a uniform emulsion; poor = did not mix easily with water, warm water (30°C), and vigorous hand shaking for 1 min was required and produced a nonuniform emulsion with visible oil-like globules present. Emulsion stability was estimated by preparing 2,400 ppm (AI) sugar ester solutions in 25°C water (30°C for xylitol dodecanoate) and classifying the ability to remain an emulsion: excellent = no separation into layers, uniform emulsion; good = layers beginning to form, but emulsifies readily upon light agitation; poor = rapidly separates into layers or oil-like globules appear, constant agitation is needed to keep the sugar ester in solution. Sugar ester concentration at which droplets freely spread upon mature pear leaves was quantified by applying 10-μl droplets with a micropipette at concentrations of 40, 200, 400, 800, 1,200, 1,800, 2,400, and 3,000 ppm (AI) (Cowles et al. 2000). Four replicates were performed for each physical characteristic. Concentration at which droplets spread on leaves were subjected to analysis of variance (ANOVA) procedures and means were separated using the Ryan-Einot-Gabriel-Welsch multiple comparison (REGW) test (SAS Institute 2000).

Initial Screening for Insecticidal Activity. The sugar esters were initially screened for insecticidal activity against second- to third- (n = 40–60) instar pear psylla, *Cacopsylla pyricola* Foerster, nymphs on pear leaves to compare relative insecticidal activities of these compounds. The sugar ester compounds were tested at a concentration of 1,200 ppm (AI) sugar ester in water and compared with a water only control. Twenty to thirty second- to third-instar pear psylla nymphs were established 24 h before treatment on individual pear leaves held in 10 dram glass vials filled with tap water. Sugar ester solutions were applied to run-off by an atomizer sprayer that delivered 25 μl solution/cm^2 leaf area. Psylla mortalities were recorded for a short 2-min and 15-min time intervals to differentiate the quick knock-down activity of the sugar esters. The experiment was designed as a randomized complete block design with four replications which was conducted in an environmental chamber with temperature and light conditions of 25 ± 2°C, 14:10 L:D with 40% RH.

Mortality data were analyzed by ANOVA and differences among treatments were determined using the REGW multiple comparison test (SAS Institute 2000). The results of each sugar ester compound's insecticidal activity was classified into none = 0%, low = 1–25%, moderate = 26–60%, or high = 61–75% to demonstrate how insecticidal patterns changed with substitutions of sugar or fatty acid components. These classifications reflected the statistical differences between treatment means.

Detailed Dosage-Mortality Relationships. After the initial screening and results on nymphal mortality were analyzed, dosage-mortality relationships of five sugar ester compounds with the highest insecticidal activity were compared. These esters were sucrose octanoate, sorbitol octanoate, sorbitol decanoate, xylitol dodecanoate, xylitol decanoate, and M-Pede insecticidal soap, evaluated at 11 concentrations (0, 40, 200, 400, 600, 1,200, 2,400, 3,200, 4,000, 8,000, and 12,000 ppm [AI] in water). The 0 ppm (AI) concentration represented a water only control that enabled insecticidal mortalities to be adjusted using Abbott's correction formula (Abbott 1925) if control mortalities exceeded 2%. The commercial insecticidal soap, M-Pede, was included to determine how the dosage-mortality relationships of sugar esters differed from insecticidal soaps. The bioassays were conducted in the same manner as the previous experiment with each treatment concentration replicated six times over time with each replicate containing 40–60 pear psylla nymphs. Nymphal mortalities were determined 15 min after treatment.

Data on dosage-mortality relationships were analyzed using ANOVA and treatment comparisons were made using the REGW test (SAS Institute 2000). Data on dosage-mortality relationships for each sugar ester were analyzed by probit analyses to determine LD_{50} and LD_{90} values (SAS Institute 2000). The probit analysis used data from each material that provided nymphal mortalities of 10–90% to obtain more accurate estimates of LD_{50} and LD_{90} values (Robertson and Preisler 1992). The confidence limits of the LD values were adjusted by the heterogeneity factor (H) if the Pearson's χ^2 indicated a significant departure from the probit model.

Insecticidal Activity to a Range of Arthropod Species. The five sugar ester compounds that were evaluated in the dosage-mortality experiment, plus M-Pede, were tested against three divergent arthropod pests: the tobacco aphid, *Myzus nicotianae* Blackman and tobacco hornworm, *Manduca sexta* (Johannson) on tobacco; and the twospotted spider mite, *Tetranychus urticae* Koch on apple. The insecticidal and miticidal activity of the sugar esters were tested at low concentrations of 400, 1,200, and 2,400 ppm (AI) in water and a water only control. In addition, sorbitol decanoate and xylitol dodecanoate, which showed little activity against *M. sexta* and *M. nicotianae* at the low concentrations, were compared with insecticidal soap at its recommended labeled rates and higher concentrations (4,000, 8,000, 12,000 ppm [AI]) for activity against the three arthropod species. The experimental design and bioassays for both experiments were conducted in the same manner as the previous experiments, except there were three replications and an *M. sexta* bioassay was developed. The *M. sexta* bioassay consisted of placing second-instar larvae (n = 20) on a 4.0 cm diameter disc of tobacco leaf within a 100-mm diameter Petri dish before treatment. Arthropod mortalities were recorded at 2-min and 15-min time intervals.

The experiment was designed as a randomized complete block design with three replications. The data were analyzed by ANOVA and differences among treatments were determined using the REGW test (SAS Institute 2000).

Results

Physical Properties of Sugar Esters. The sugar ester compounds we synthesized differed in physical properties (Table 1). Only sucrose octanoate and sorbitol octanoate mixed readily with water although those materials rated as having good solubility mixed easily with water after vigorous shaking. Xylitol dodecanoate existed as a soft solid material that did not easily emulsify with water, but once emulsified, had surprisingly good leaf wetting properties. Analysis of leaf wetting ability showed significant differences among sugar esters (F = 118.8, df = 6, 18; P = 0.0001). There was no obvious relationship between a material's solubility in water, emulsion stability and droplet spread on pear leaves and hydrophilic-lipophilic balance (HLB). Sucrose octanoate and sorbitol octanoate were unique in that they readily mixed with water and formed stable emulsions. These two compounds also exhibited good surfactant properties by having droplets spread at low concentrations of 40–200 ppm. Xylitol dodecanoate could also wet leaves at a concentration of 40 ppm, yet this material was difficult to keep in solution and quickly separated from water. The remaining compounds had good water solubility, but needed constant agitation in order for serial dilutions to be made and for solutions to be applied.

Initial Screening. The effects of sugar ester treatments on psylla mortality (Table 2) were significantly affected by treatment (F = 33.5, df = 7, 45; P < 0.0001), time (F = 74.2, df = 1, 45; P < 0.0001), and time by treatment interaction (F = 5.7, df = 7, 45; P < 0.0001). Although most nymphs appeared to become paralyzed or killed immediately after treatment, some nymphs curved the tips of their abdomens upward in an apparent attempt to keep the spiracles above the film of solution on the leaf. Many nymphs died with their abdomens extended upward when sprayed with toxic concentrations of sugar ester, whereas, nymphs did not display this behavior when they were sprayed with an ineffective sugar ester concentration. Treated leaves dried within the 2-min time period after treatment and approximately half of the mortality occurred at that time in comparison to the 15-min time period except for materials that showed no insecticidal activity. In our preliminary bioassays, psylla nymphal mortality did not change significantly between 15 min and 24 h after application of sugar esters (G.J.P., unpublished data).

Sucrose octanoate, sorbitol octanoate, and xylitol decanoate applied at 1,200 ppm produced relatively high psylla mortalities in comparison to the other

Table 1. Physical characteristics of the sugar ester compounds

Sugar ester compound	CAS registry no.[a]	Chemical index name	Color	Physical state	Solubility with Water[b]	Stability of a 2,400 ppm emulsion[c]	Conc. (ppm ± SE) for droplet spread[d]	HLB[e]
Sucrose octanoate	42922-74-7, 58064-47-4	α-D, Glucopyranoside β-D-fructofuranosyl octanoate	Dark amber	Liquid	Excellent	Excellent	80.0 ± 40.0 d	22.0
Sorbitol octanoate	108175-15-1	D-Glucitol octanoate	Dark amber	Liquid	Excellent	Excellent	160.0 ± 40.0 d	15.8
Xylitol octanoate	–	–	Dark amber	Liquid	Good	Poor	2550.0 ± 150.0 a	11.8
Sorbitol hexanoate	50809-54-6	D-Glucitol hexanoate	Dark amber	Liquid	Good	Poor	2100.0 ± 300.0 b	16.8
Xylitol dodecanoate	211867-92-5	Xylitol dodecanoate	White	Solid	Poor	Poor	80.0 ± 40.0 d	9.9
Sorbitol decanoate	108175-14-0	D-Glucitol decanoate	Dark amber	Liquid	Good	Good	1500.0 ± 300.0 c	14.9
Xylitol decanoate	–	–	Dark amber	Liquid	Good	Poor	160.0 ± 40.0 d	10.8

[a] Chemical Abstracts Service (CAS) registry number for compounds that have been synthesized at least once. Those compounds without a CAS number represent a newly synthesized compound.
[b] Ability to dissolve readily with 25°C water when making a concentration of 2,400 ppm.
[c] Ability to remain an emulsion without separating into layers for 1 min after mixing a concentration of 2,400 ppm in 25°C water (30°C) for xylitol dodecanoate.
[d] Concentration at which a 10-μl droplet spread when applied directly to a mature pear leaf. Means within a column followed by the same letter are not significantly different, Ryan-Einot-Gabriel-Welsch multiple comparison (REGW) test, $P > 0.05$ (SAS Institute, 2000).
[e] Hydrophilic/lipophilic balance.

Table 2. Comparison of *C. pyricola* nymphal mortalities to different sugar ester-fatty acid compositions 2 and 15 minutes after applying 1,200 ppm AI solutions

Treatment	Percent Kill (±SE)	
	2 min	15 min
Untreated control	0.0 ± 0.0bA	0.0 ± 0.0fA
Sucrose octanoate	25.3 ± 9.3aA	71.8 ± 7.7aB
Sorbitol octanoate	25.6 ± 2.7aA	58.3 ± 4.8bB
Xylitol octanoate	0.0 ± 0.0bA	15.9 ± 2.8eB
Sorbitol hexanoate	0.0 ± 0.0bA	0.0 ± 0.0fA
Xylitol dodecanoate	11.5 ± 3.0abA	34.4 ± 6.0cB
Sorbitol decanoate	0.0 ± 0.0bA	25.0 ± 4.8dB
Xylitol decanoate	32.1 ± 5.1aA	73.1 ± 8.1aB

Means within columns followed by the same lowercase letter or means within rows followed by the same uppercase letter are not significantly different, $P > 0.05$, REGW test (SAS Institute 2000).

sugar esters at both the 2-min ($F = 6.7$, df = 7, 21; $P < 0.0003$) and 15-min time intervals ($F = 32.4$, df = 7, 21; $P < 0.0001$ (Table 2). Xylitol dodecanoate and sorbitol decanoate expressed lower psylla mortalities (25.0–34.4%), whereas xylitol octanoate and sorbitol caproate had little or no activity. Percent nymphal mortalities (Table 2) were negatively correlated with droplet spread on pear leaves which is directly associated with leaf wetting ($R^2 = 0.73$; $y = 60.56x - 0.022$; $F = 13.7$; df = 1, 5; $P = 0.014$). Furthermore, we found no correlation ($R^2 = 0.03$; $y = 21.44x - 1.25$; $F = 0.18$; df = 1, 5; $P = 0.69$) between HLB (Table 1) and psylla mortalities (Table 2).

The structure-function relationships of how sugar and fatty acid substitutions affect sugar ester insecticidal activity to psylla nymphs is summarized in Table 3. No definitive pattern of insecticidal activity of sugar ester compounds was evident when sequentially altering the sugar or fatty acid components from lower to higher numbers of carbon atoms (molecule size), or when altering the size of the sugar molecule. In sugar ester compounds containing a C_8 fatty acid (octanoate), insecticidal activity progressively increased when the sugar component increased from a C_5 (xy-

Table 3. Summary of how alterations sugar ester components affected insecticidal activity of materials applied at 1,200 ppm AI to *C. pyricola* nymphs

Constituent change	Sugar (carbon atoms)	Fatty acid (carbon chain length)	Insecticidal activity (% nymphal mortality)
Carbohydrate	xylitol (5)	octanoate (8)	low (15.9)
	sorbitol (6)	octanoate (8)	moderate (58.3)
	sucrose (12)	octanoate (8)	high (71.8)
	xylitol (5)	decanoate (10)	high (73.1)
	sorbitol (6)	decanoate (10)	low (25.0)
Fatty Acid	xylitol (5)	octanoate (8)	low (15.9)
	xylitol (5)	decanoate (10)	high (73.1)
	xylitol (5)	dodecanoate (12)	moderate (34.4)
	sorbitol (6)	hexanoate (6)	none (0.0)
	sorbitol (6)	octanoate (8)	high (58.3)
	sorbitol (6)	decanoate (10)	low (25.0)

Categories of none = 0%, low = 1–25%, moderate = 26–57%, or high = 58–75% nymphal mortalities based on significant statistical differences among sugar ester materials as shown in Table 2.

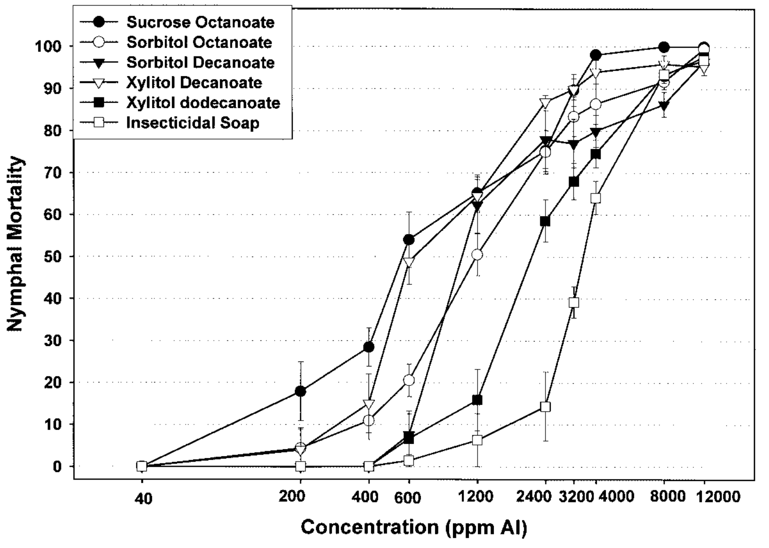

Fig. 1. Dosage-mortality curves for sugar ester compounds and insecticidal soap (M-Pede) applied at various concentrations to pear psylla nymphs on pear leaves 15 min after application.

litol) to a C_6 (sorbitol) reduced sugar to a C_{12} disaccaride (sucrose). Quite the opposite occurred for the C_{10} fatty acid esters (decanoate), which showed a decrease in insecticidal activity when the sugar component increased from C_5 to C_6 reduced sugar.

More of a discernible pattern for insecticidal activity was evident when the sugar component was held constant and the fatty-acid component was sequentially increased (Table 3). Xylitol or sorbitol based sugar esters produced insecticidal patterns that went from low activity with lower carbon chain fatty acids, to peak activity with mid-ranged carbon chained fatty acids, and then declined with higher carbon chain fatty acid substitutions. For example, insecticidal activity for xylitol was lowest for octanoate (C_8), high for decanoate (C_{10}), and moderate for dodecanoate (C_{12}) fatty acid substitutions.

Dosage-Mortality Relationships. Pear psylla nymphal mortalities (Fig. 1) were significantly affected by sugar ester treatment ($F = 7.6$, df = 6, 269; $P < 0.0001$), concentration ($F = 15.7$, df = 9, 296; $P < 0.0001$), and concentration by treatment interaction ($F = 9.0$, df = 39, 269; $P < 0.0001$). Sucrose octanoate had higher insecticidal activity than the other materials at concentrations of 200 ($F = 59.7$, df = 5, 25; $P < 0.0001$) and 400 ppm ($F = 569.7$, df = 5, 25; $P < 0.0001$). Most of the sugar esters performed similarly at concentrations between 600 and 2,400 ppm except for xylitol dodecanoate and insecticidal soap which had much lower levels of insecticidal activity.

The slopes and LD values from the probit analyses differed among the sugar ester and insecticidal soap materials as determined by overlapping confidence limits (Table 4). All of the sugar esters and insecticidal soap had high Pearson's χ^2 values which indicated a significant departure from the probit model. Examination of the residuals revealed that these departures were mainly because of the lack of psylla mortality at lower concentrations followed by rapidly increasing morality at higher concentrations (e.g., xylitol dodecanoate, insecticidal soap), a poor mortality response to increasing concentration at the high end of the dosages (xylitol decanoate, sorbitol octanoate) or both (e.g., sorbitol decanoate). Sucrose octanoate, sorbitol octanoate, and xylitol decanoate produced significantly higher psylla mortalities than the other

Table 4. Comparisons among sugar ester and insecticidal soap toxicities to *C. pyricola* nymphs on pear leaves based on a probit analysis

Treatment	n	Slope (95% CL)	LC_{50} (95% CL)[a]	LC_{90} (95% CL)[a]	Pearson's χ^2 (df = 4)[b]
Sucrose octanoate	48	3.13 (2.44–3.81)ABC	2124 (1691–2576)B	10680 (7973–16386)B	166.6*
Sorbitol octanoate	54	3.41 (2.71–4.12)AB	3107 (2449–3786)AB	13655 (10591–17659)B	298.6*
Sorbitol decanoate	54	1.83 (1.04–2.62)C	3523 (2730–4302)A	32189 (19407–62929)A	445.7*
Xylitol decanoate	48	4.39 (3.62–5.15)A	2103 (1800–2419)B	6650 (5509–8544)B	152.2*
Xylitol dodecanoate	48	2.43 (1.25–3.60)BC	5926 (2820–6719)A	39436 (21250–22132)A	387.0*
Insecticidal soap	48	2.72 (1.26–4.17)BC	7828 (5360–14177)A	50269 (22440–70052)A	783.3*

Means within columns followed by the same letter had overlapping confidence limits and are not significantly different (probit analyses, SAS Institute 2000).

[a] Concentrations are given in ppm AI material in water.

[b] Pearson's χ^2 followed by an asterisk are significant at $P = 0.10$, df = $n - 1$ (SAS Institute 2000).

Table 5. Arthropod mortalities 15 min after application of sugar esters at a low range of concentrations

Treatment	% Conc. (ppm AI)	Percent mortality (±SE)		
		M. sexta	*M. nicotianae*	*T. urticae*
Untreated control	0.00	0.0 ± 0.0cA	0.0 ± 0.0gA	0.0 ± 0.0cA
Sucrose octanoate	400	3.3 ± 1.7cC	71.6 ± 5.0bB	97.4 ± 1.9aA
	1,200	26.7 ± 4.4bC	79.7 ± 3.9bB	100.0 ± 0.0aA
	2,400	41.7 ± 10.1aB	98.5 ± 1.1aA	100.0 ± 0.0aA
Sorbitol octanoate	400	3.3 ± 3.3cB	4.2 ± 1.2gB	84.9 ± 7.3bA
	1,200	0.0 ± 0.0cC	21.6 ± 1.2defB	96.2 ± 4.8aA
	2,400	3.3 ± 3.3cC	51.4 ± 9.0cB	100.0 ± 0.0aA
Xylitol decanoate	400	1.7 ± 1.7cB	8.5 ± 1.5fgB	81.6 ± 4.7bA
	1,200	0.0 ± 0.0cC	25.8 ± 4.0deB	100.0 ± 0.0aA
	2,400	0.0 ± 0.0cC	29.9 ± 1.6dB	100.0 ± 0.0aA
Xylitol dodecanoate	400	0.0 ± 0.0cC	29.1 ± 3.7deB	100.0 ± 0.0aA
	1,200	0.0 ± 0.0cC	35.2 ± 6.2dB	100.0 ± 0.0aA
	2,400	0.0 ± 0.0cC	34.9 ± 2.6dB	100.0 ± 0.0aA
Sorbitol decanoate	400	0.0 ± 0.0cC	9.8 ± 2.1efgB	100.0 ± 0.0aA
	1,200	0.0 ± 0.0cC	32.6 ± 8.5dB	100.0 ± 0.0aA
	2,400	0.0 ± 0.0cC	71.6 ± 5.0bB	100.0 ± 0.0aA

Means within columns followed by the same lowercase letter or means within rows followed by the same uppercase letter are not significantly different, $P > 0.05$, REGW test (SAS institute 2000).

sugar ester compounds or insecticidal soap, based on LD_{90} values. The probit analyses determined that the dosage-mortality curves for sorbitol decanoate and xylitol dodecanoate were similar to insecticidal soap in reference to psylla mortalities.

Toxicity to a Range of Arthropod Species. Insect mortalities for the low range of sugar ester concentrations (Table 5) were significantly affected by arthropod species ($F = 1{,}716.3$, df = 2, 166; $P < 0.0001$), sugar ester treatment ($F = 55.6$, df = 5, 166; $P < 0.001$), and treatment concentration ($F = 134.4$, df = 3, 166; $P < 0.0001$). All interactions between arthropod species, sugar ester treatment, and treatment concentration were significant ($P < 0.0001$). *M. sexta* mortalities were lowest of the insect species and only sucrose octanoate at the higher concentrations of 1,200 and 2,400 ppm produced significantly higher mortalities than the other materials ($F = 19.0$, df = 15, 44; $P < 0.0001$). *M. nicotianae* mortalities on tobacco (Table 5) closely followed those of *C. pyricola* on pear (Table 2). Sucrose octanoate and sorbitol decanoate yielded significantly higher *M. nicotianae* mortalities than the other materials ($F = 77.4$, df = 15, 44; $P < 0.0001$). *T. urticae* was the most susceptible arthropod species to the sugar ester materials which yielded mortalities ranging from 88.8 to 100%.

Higher concentrations of 4,000, 8,000, and 12,000 ppm were explored for xylitol dodecanoate and sorbitol decanoate to determine their toxicities to the three arthropod species relative to insecticidal soap, which is typically applied at rates of 4,900–9,800 ppm for soft bodied insect control (Table 6). Xylitol dodecanoate and sorbitol decanoate were selected because they had no toxicity to *M. sexta* and low or moderate toxicity, respectively, to *M. nicotianae* (Table 5). Arthropod mortalities were significantly affected by concentration ($F = 26.9$, df = 3, 66; $P < 0.0001$), arthropod species ($F = 305.4$, df = 2, 66; $P < 0.0001$), and treatment by insect interaction ($F = 45.8$, df = 4, 66; $P < 0.0001$). However, the treatment by concentration interaction was not significant for the range of concentrations tested ($F = 0.0$, df = 3, 66; $P < 0.0001$), which indicated a lack of response in mortality as concentrations increased. Therefore, arthropod mortalities were averaged across concentrations for each insect by treatment combination. Low *M. sexta* mortalities were obtained from both sugar esters and insecticidal soap when applied at these high concentrations, although xylitol dodecanoate and insecticidal soap produced significantly higher mortalities than sorbitol decanoate, which essentially had no activity against this insect ($F = 15.0$, df = 3, 24; $P < 0.0001$). Both sugar esters provided high *M. nicotianae* mortalities compared with insecticidal soap ($F = 17.3$, df = 3, 24; $P < 0.0001$), whereas all three materials produced >94% *T. urticae* mortalities ($F = 1, 141.3$, df = 3, 24; $P < 0.0001$).

Discussion

We have demonstrated that altering the sugar or fatty acid component of sugar ester compounds will alter the insecticidal activity of a sugar ester compound (Tables 2–4). Little information is available on how the sugar component actually influences the insecticidal activity of sugar ester, even though it serves as the backbone of this compound. Sugar structures contain free hydroxyl groups that serve as sites for fatty acid esterification. Disaccharides (e.g., sucrose) have more free hydroxyl sites that give rise to a mixture of sugar ester isomers, but differing methods of

Table 6. Arthropod mortalities averaged over treatment concentrations of 4,000, 8,000, and 12,000 ppm AI, 15 minutes after application

Treatment	Percent mortality (±SE)		
	M. sexta	*M. nicotianae*	*T. urticae*
Untreated control	0.0 ± 0.0bA	0.0 ± 0.0cA	0.0 ± 0.0bA
Xylitol dodecanoate	16.1 ± 1.4aC	70.0 ± 6.4aB	100.0 ± 0.0aA
Sorbitol decanoate	1.6 ± 1.2bB	94.8 ± 2.9aA	100.0 ± 0.0aA
M-Pede soap	11.7 ± 2.5aC	37.4 ± 6.8bB	97.2 ± 1.6aA

synthesis can produce sucrose esters high in monoester (Farone and Serfass 1998) or diester content (Chortyk et al. 1996). Natural sugar ester extracts from certain *Nicotiana* spp. contain a mixture of both sucrose and glucose esters (Matsuzaki et al. 1992, Severson et al. 1994), which have excellent insecticidal properties (Puterka and Severson 1995, Liu et al. 1996), yet sucrose esters and their synthesis have been the primary focus of insecticidal study (Buta et al. 1993, Chortyk et al. 1996). Our study indicated that changing the sugar component greatly influenced insecticidal activity and that high insecticidal activity could be achieved with sugars by modulating the fatty acid chain length (Table 3). Previous research established that the fatty acid component also has profound effects on the insecticidal properties of sugar esters. Chortyk et al. (1996) determined that sucrose esters containing C_7 and C_8 fatty acids produced high *M. nicotiana* mortalities, whereas C_6 and C_{9-12} fatty acids produced much lower mortalities. We discovered that different sugar bases (xylitol, sorbitol) influenced which fatty acid carbon chain length produced the greatest insecticidal activity. Insecticidal activity peaked at fatty acid chain lengths of C_8 or C_{10}, depending upon the sugar backbone (Table 2 and 3). If insecticidal activity could be simply explained as a surfactant relationship one would expect a certain HLB would hold. Thus, decreasing the size of the hydrophile from sorbitol (C_6) to xylitol (C_5) would require a decrease in size of the lipophile to maintain the same HLB relationship (Adamson 1976). Quite the opposite was the case for sugar esters in which increasing the size of the hydrophile as indicated above required an increase in lipophile size to maintain an HLB of 10.8–11.8 (Table 1). With regard to the degree of esterification of sucrose esters, it has been established that monoacyl sucrose ester produced low *M. nicotiana* mortalities on tobacco leaves, whereas diacyl sucrose esters of C_7 and C_8 fatty acids resulted in high mortalities (Chortyk et al. 1996). In contrast, our studies demonstrated that C_8 sucrose esters high in monoester content provided high levels of mortality against *C. pyricola, M. nicotiana,* and *T. urticae,* regardless of leaf type (Tables 2 and 5). Moreover, several of the sorbitol and xylitol esters (sorbitol octanoate, xylitol decanoate) had relatively high levels of activity against the aforementioned arthropods. Our results indicate that changes in either the sugar or fatty acid component of sugar esters lead to unpredictable effects on insecticidal activity that can only be determined by empirical tests.

Sugar esters have excellent surfactant and emulsifier properties that are desirable to the food and cosmetics industry, but also share a number of insecticidal properties with other surfactants. Initial insect bioassays (Table 1) and dosage-mortality data (Table 4) revealed that sucrose octanoate, xylitol decanoate, and sorbitol octanoate were most toxic to *C. pyricola* nymphs. These compounds varied in their solubility in water and in emulsion stability, yet droplet spread on pear leaves was achieved at low concentrations of 80–160 ppm (Table 1) and was strongly correlated with psylla mortalities (Table 2). Droplet spread is related to leaf wetting, which is closely associated with surface tension values. It is of importance to note that the droplet spread for the sugar ester solutions on pear leaves occurred at far lower concentrations than the concentration needed to uniformly wet the leaf and kill arthropod pests. Sugar ester materials applied at concentrations that produced >70% psylla mortalities also uniformly wet the leaf, whereas lower concentrations produced only partial coverage because the droplets failed to coalesce. We lacked the equipment needed to determine surface tension and other properties of our sugar ester compounds in solution. However, studies have shown that the insecticidal and miticidal activity of surfactants are correlated with surface tension values <30 mN/m (Imai et al. 1994) and leaf wetting at low concentrations of 50–300 ppm (Cowles et al. 2000). Sugar ester HLB did not correlate with insect mortalities, which was also found to be true for a large range of surfactants tested by Imai et al. (1994). Sugar esters (Xia et al. 1997) share another property with surfactants, including insecticidal soaps (Imai et al. 1995), in that higher humidities increase insecticidal activity by increasing the duration of wetting. Imai et al. (1995) proposed that insecticidal surfactants require low surface tension to spread readily upon insect cuticles and that increasing wetting time increases the probability that the insect will suffocate. Although surfactants must readily spread over an insect cuticle, their interaction with the host plant cuticle also plays a key role in the suffocation process. Cowles et al. (2000) has demonstrated that miticidal activity of Silwet L-77 on strawberry was significantly less than on kidney bean and suggested this may have resulted from differences in the ability of Silwet L-77 to wet these leaf surfaces. Surfactant performance is influenced by plant surfaces through complex interrelated physiochemical factors that include cuticle roughness, presence of trichomes, trichome type, and cuticular hydrocarbons (Halloway 1970). It is not known how hydrophobic insect cuticles are or how closely related the hydrophobicity or wettability of insect cuticles are to their respective host plants. Surface active materials that wet leaves readily at one concentration may require higher concentrations to wet the target insect. Clearly, leaf wetting is only one factor affecting the insecticidal activity of sugar esters. Our data on two insect species, *M. nicotiana* and *M. sexta,* on tobacco (Table 5) demonstrates that even with thorough wetting of the leaf *M. nicotiana* mortalities were high but *M. sexta* mortalities were very low, suggesting that other factors specific to the insect are in play. Certainly, more research is needed on characterizing the surface-active properties of sugar esters and their relationship to the physiochemical interactions between the leaf and insect before we can arrive at an understanding of the mechanisms of insecticidal action and how sugar ester performance can be improved.

The underlying mechanisms of insecticidal action of sugar esters, or surfactants and soaps for that matter, is subject to much speculation but little study. Sugar esters contain lipophilic acyl chains and free hydroxyls, which give them soaplike properties (Neal et al. 1994). Two main theories of insecticidal action for soaps that were presented in the early 1900s and still remain controversial today include (1) insects suffocate when soap produces mechanical occlusions of the body openings; or (2) the insects become desiccated by the caustic properties of the free alkaline constituents of soaps upon the insect's cuticle. These theories were challenged by Siegler and Popenoe (1925) who presented data showing that the free fatty acids are themselves the toxic agents and they believed that the fatty acids were absorbed through the insects cuticle and act upon the insects cellular membranes. Soaps that are alkali salts of fatty acids undergo partial hydrolysis when mixed with water, which results in free alkali and free fatty acids. Research by Puritch (1975) further supports this idea. He found fatty acids of soaps can disrupt cellular membrane integrity in insects. Certainly, fatty acids themselves are known to be insecticidal and their activity is greatly increased through saponification or esterification (Kabara 1987). Yet, others maintain that suffocation is the likely mechanism because of the highly wettable nature of soaps and other surfactant solutions (Imai et al. 1994). Sugar ester structure does not lend itself to hydrolysis during the short time-frame when it is applied and kills insects. Therefore, it is doubtful that direct toxicity to insects from free fatty acids is an plausible mechanism for sugar esters. From our data we agree that suffocation is possible because wetting of the leaf is needed before insect mortalities occur. However, as we already stated, leaf wetting does not always lead to insect mortality, as was the case for *M. sexta*. Furthermore, in an earlier study (Puterka and Severson 1995) dry sugar ester residues on pear leaves caused high mortalities in newly eclosed *C. pyricola* nymphs that contacted treated leaf surfaces. The dead nymphs appeared to be swollen with water, which supported the idea that disruption of the cuticle or cellular membranes occurred. Sugar esters will naturally break down as a result of microbial action hours after application, in which case free fatty acid may affect the insect cuticle. From the current body of information on mechanisms and from our study, it seems likely that more than one mechanism can be involved, depending on the insect's surface chemistry, surface structure, and other specialized structural and physiological adaptations that have evolved to enable a particular insect species to occupy a specific niche or environment.

Studies on natural sugar esters obtained from trichome exudates or leaf extractions from *N. gossei* have established they are effective against *M. sexta* (Parr and Thurston 1968) *C. pyricola* (Puterka and Severson 1995), mites, and a variety of aphids and whiteflies (Buta et al. 1993, Neal et al. 1994, Severson et al. 1994, Liu et al. 1996). Neal et al. (1994) reported that natural sugar esters extracts were not effective against the western flower thrips *Frankliniella occidentalis* (Pergande) or the Colorado potato beetle *Leptinotarsa decemlineata* (Say). Synthetic diesters of sucrose octanoate have been less tested and efficacy reports are limited to aphids and whiteflies (Chortyk et al. 1996, Xia et al. 1997, Liu et al. 1996). The monoacyl sugar ester compounds we examined varied considerably in toxicity to the range of arthropod species we examined. Sucrose octanoate was the only material that was effective against the range of arthropod pests on different leaf types at concentrations of 1,200–2,400 ppm (Table 2 and 5). No single chemical structure for the xylitol or sorbitol esters were optimally effective against the range of arthropods at these concentrations and sorbitol octanoate and xylitol decanoate showed the greatest insecticidal activity of this group. Xylitol decanoate produced high *C. pyricola* mortalities on pear at 1,200–2,400 ppm, but showed low activity against *M. nicotiana* and no activity against *M. sexta* on tobacco. In contrast, sorbitol decanoate at these concentrations produced low *C. pyricola* mortalities on pear, yet ranked second in *M. nicotiana* mortality and was not active against *M. sexta* on tobacco. All of the sugar ester materials produced high *T. urticae* mortalities on pear at very low concentrations of 400 ppm. Those sugar esters with no insecticidal activity to *M. sexta* (xylitol dodecanoate, sorbitol decanoate) at concentrations of 2,400 ppm (Table 5) still produced very low mortalities when concentrations were increased to as high as 12,000 ppm (Table 6). Yet, even these two sugar ester compounds with the lowest insecticidal activity of those we synthesized outperformed the insecticidal soap (Fig. 1; Table 6). These results expand the list of insects that are susceptible to sucrose octanoate and establishes one new compound, xylitol decanoate, as having notable insecticidal and miticidal activity.

Further characterization of the physical and chemical properties of sugar ester compounds, testing sugar esters against a broader range of arthropod species, and in-depth research into the mechanisms-of-action for sugar esters against arthropods and how these mechanisms are affected by different arthropod and plant surfaces are needed to better understand how sugar ester chemistry can be improved. We have established that sucrose octanoate high in monoester content has the broadest insecticidal activity of the sugar esters we produced. Our study has shown that changes in the fatty acid and sugar components of sugar esters produces unpredictable levels of insecticidal activity and also affects the range of arthropods that sugar ester compounds are effective against. We produced sugar ester compounds with toxicity to a broad range of arthropod species (sucrose octanoate) or narrow range of species (sorbitol decanoate) and synthesized a new sugar ester compound that is effective against psylla and mites. Sugar ester chemistry presents a special opportunity in which compounds could be designed to fit particular crop pest needs. This chemistry may be of particular interest today where safety to humans and the environment are an issue. Another important quality of sugar esters is that to date we have not observed phytotoxicity to many types of plant species at concentrations that are effective against mites and aphids, which can be of concern when using insecticidal soaps. Sugar ester residues break down rapidly through microbial action in the environment into their base components, are already internationally approved as a food ingredient, and a new sugar ester manufacturing process has been developed that produces no toxic by-products (Farone et al. 2002). Recently, sucrose octanoate was registered as AVACHEM Sucrose Octanoate (AVA Chemical Ventures, L.L.C., Portsmouth, NH) with the United States Environmental Protection Agency for control of insect and mite pests on all agricultural crops and ornamentals, and for greenhouse use. This registration will aid in determining the practical utility of this pesticide chemistry by enabling diverse testing against arthropod pests in numerous crops and environmental conditions.

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